

EFFECTS OF CHLORINE IN COAL ON BOILER SUPERHEATER/REHEATER CORROSION

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Abstract

Many British studies have correlated superheater/reheater corrosion in pulverized coal boilers with the total chlorine (Cl) content in coals, which has led many US boiler manufacturers to set their maximum recommended Cl level at 0.3%. However, Cl-related boiler corrosion has not been reported by US utilities burning high-Cl Illinois coals. Other factors, such as boiler parameters, have been studied for their effect on corrosion rate. This study measured the rate of corrosion caused by two high-Cl coals (British and Illinois) and one low-Cl Illinois coal under identical pilot-scale combustion conditions for a duration which would give reliable comparisons. The results showed no correlation between coal Cl content and rate of corrosion, but showed a correlation between the rate of corrosion and the metal temperature used. These data could provide a basis for lifting the limit of burning high chlorine Illinois coals in the utility boilers.

Introduction

Many British studies have correlated accelerated fireside corrosion of heat exchanger tubes in utility boilers with the high-Cl content in coal (Raask, 1963; Reid, 1971; Meadowcroft and Manning, 1983). Their correlations implied that the corrosion rate of boiler tubes increased proportionally with increasing Cl concentration in the coal. Based on these correlations, US boiler manufacturers and utility operators consider coals containing more than 0.3% Cl to be potentially corrosive and have set guidelines on the Cl content (<0.3%) of coal to be used in their boilers. These guidelines were based primarily on extrapolation British coal data to predict the probable corrosion behavior of US coals. The guidelines on the Cl level have discouraged the burning of high-Cl Illinois Basin coals in utility boilers.

A survey conducted jointly by Electric Power Research Institute and Illinois Clean Coal Institute during 1992 (Doane et al., 1994; Wright et al., 1994) indicated that some US utilities have decades of experience burning high-Cl coals in pulverized coal (PC) fired boilers. Although fireside corrosion problems have been reported, none of them could be directly related to the presence of Cl in coal. This contradiction with published data suggested that the role of Cl in coal on boiler-tube corrosion was not fully understood. It is possible that the level of Cl in coal is not as harmful as predicted, or the corrosivity of high-Cl Illinois coal is less severe than that of British coal, or other coal properties such as sulfur and potentially volatile alkali metals in coals are possibly associated with boiler corrosion (Chou et al. 1998). The differences in boiler design and operation between US and UK utilities, such as boiler superheater/reheater temperatures, might also have attributed to this discrepancy.

This study focuses on how the corrosivity of a high-Cl Illinois coal compares with that of a British coal with a similar Cl content at superheater/reheater temperatures. Three pilot-scale combustion tests were conducted. The rates of corrosion caused by two high-Cl coals (British and Illinois) and a low-Cl baseline Illinois coal were measured under identical combustion conditions for a duration which would give a reliable comparison. The corrosion tests used Alloy 304SS which is a frequently used material at the hottest superheater section of both US and UK utility boilers. The corrosivity data from a temperature range including two specific metal temperatures, 1100°F and 1200°F were determined. The cooler metal temperature is common in the US boilers and the hotter temperature is common in the UK boilers.

Experimental

Coal samples - During sample acquisition, the available high-Cl British coals from the British Coal

Corporation Coal Research Establishment (CRE) coal sample bank were obtained for screening analysis (CRE, 1993). One of the coals obtained had a chlorine content (~0.4%) comparable to that of the high-Cl Illinois coal chosen. This British coal is also currently the most mined coal. A 20-ton lot of the British coal, therefore, was purchased from RJB Mining in Great Britain and shipped to the US for the combustion test. To form a basis for assessing the corrosion effect of the two high-Cl coals, a low-Cl Illinois coal was included in the combustion tests. Splits of the 20-ton lots of the three coals were analyzed for chlorine, sulfur, and ash content using the ASTM methods (1994).

Pilot scale combustion test - A refractory-lined, stoker-fired Fireside Corrosion Test Facility at McDermott Technologies, Inc. in Alliance, Ohio was used to burn the coal. A variable-speed screw feeder supplied the coal to the bottom of the stoker combustion chamber. A forced draft fan provided the primary air that entered the furnace through tuyers surrounding the burner. Penetrations right above the combustion chamber were used to accommodate the corrosion probes. Two sets of probes were used to approximate US and UK boiler tube wall temperatures. One set was regulated to include the temperature of 1200°F (649°C) which is common in UK boilers, and the other set was regulated to include the temperature of 1100°F (593°C) which is common in US boilers. A frequently used commercial alloy at the hottest superheater section of utility boilers was used to fabricate the corrosion probes. The ASTM designation of this alloy is SA213-T304 (304SS). The nominal composition of 304SS is given in Table 1. The essential features of the test matrix are given in Table 2.

High-temperature corrosion probe designation - Tube samples of the alloy in a dimension of 1" in outside diameter by 0.94" in length were fabricated and placed in series (Figure 1). The ends of each tube segment were shaped to extrude and concave chamfers at 10° and 45°, respectively. The chamfers allowed multiple segments to be assembled on the corrosion probe with an air-tight seal. A mechanical force was applied to the ends of the probes so that a tight fit could be achieved. Duplicate samples of the alloy were included in the corrosion probes. Type-K thermocouples were attached to one of the tube samples through the inner surface of the probes. The thermocouple junctions were positioned in EDM-drilled holes inside the samples facing the flue gas. Room-temperature compressed air was used to cool the corrosion probes and maintain the metal temperatures. Flow rate of the cooling air was regulated automatically by a controller that responded to the set points of the probe temperatures.

Corrosion rate measurements - The initial weight and initial outer diameter of each tube sample were measured. In addition, the wall thicknesses were carefully measured around the perimeter of each sample at eight points. The points were identified as 12:00, 1:30, 3:00, 4:30, 6:00, 7:30, 9:00, and 10:30 positions, with the 12:00 position being the leading edge facing the flue gas (Figure 2). After fireside corrosion exposure was completed, it was found that metal wastage on the inner surface of the tube samples were negligible, so only outside diameters of the tube samples were measured. All measurements were made in the middle section of the tube samples.

After the corrosion exposure, one of the duplicate samples was chemically cleaned. The chemical cleaning removed the coal ash deposit and scale formed on the sample surfaces during the exposure. After the cleaning, the final weight was again measured. Based on the total weight changes and initial surface areas, the average corrosion rates of the alloy were calculated. The wall thicknesses of the chemically cleaned samples were also measured at the same positions mentioned above. As a result, the corrosion wastage of the tube samples could be determined, which were subsequently used to calculate the local corrosion rates. The corrosion rates for the two high-Cl coals were extrapolated from the 1000-hour test result and reported as mils per year (mpy). Because of equipment difficulty during the low-Cl coal test, the sample was only combusted for 813 hours. The data, however, were again extrapolated and reported in mpy for comparisons with the other coals.

Cross sectional examination - A cross-section was prepared metallographically from one of the alloy samples after the corrosion exposure. The sample was mounted in Bakelite, cut, and polished dry to preserve any water-soluble compounds that might exist on the alloy surfaces. The ash and scale layers of the sample from each test were examined under an optical microscope and a scanning electron microscope (SEM) equipped with energy dispersive X-ray (EDX) analytical capability. The remaining metal thicknesses of the samples were also determined using a Nikon Microscope at the eight positions as described before.

Results and Discussion

Chemical composition of the three coal samples - Splits of the 20-ton lots of the three coals were analyzed for chlorine, sulfur, and ash content (Table 3). The two high-Cl coals contained medium-

sulfur contents; whereas, the low-Cl Illinois coal contained high-sulfur content. Also, the as-shipped Illinois high-Cl coals had much less ash than did the British high-Cl coal.

Pilot Scale Combustion - Rate of Corrosion

Three long-term, pilot-scale combustion tests were conducted using SA213-T304 (304SS) to evaluate boiler corrosion produced at two specific boiler wall temperatures. The corrosion rate was most pronounced at the 1:30, 3:00, 9:00, and 10:30 positions; in other words 30 to 90° from the leading edge (Figure 2). These measurements were extrapolated to the amount of corrosion in one year or mils per year (mpy).

High-Cl Illinois coal - In general, the corrosion rates at the leading edge (12:00 position) were less than those measured at 30 to 90° away from the leading edge. For example, the corrosion rate of 304SS at 1100°F at the 12:00 position was approximately 40 mpy (not shown), while the greatest corrosion rate between 30 to 90° positions was greater than 100 mpy (shown in Figure 3). Such variation was consistent with the general observation of superheater corrosion in the field. The changes for the corrosion rate with respect to metal temperature at the positions between 30 to 90° are shown in Figure 3. The corrosion rate of 304SS within the temperature range analyzed appeared to show an earlier stage of a bell-shape relationship. It showed increases with increasing metal temperature; and the increases in the corrosion rate were quite significant. For example, the corrosion rate was approximately 120 mpy at 1100°F, and about 260 mpy at 1200°F.

High-Cl British coal - Similarly, the corrosion occurring on the probes at the 30 to 90° locations was more severe than that at the leading edge. The changes of corrosion rate at the positions between 30 to 90° locations with respect to increasing metal temperature are shown in Figure 4. The corrosion rate, similar to what was seen in the test for the high-Cl Illinois coal, increased consistently with increasing metal temperature; and the increases in the corrosion rate were quite significant. The corrosion rate was about 190 mpy at 1100°F, and about 267 mpy at 1200°F.

Low-Cl Illinois coal - As usual, the corrosion occurring on the probes at the 30 to 90° locations was more severe than at the leading edge. The changes of corrosion rate between the 30 to 90° positions with respect to increasing metal temperature are shown in Figure 5. Similar to the tests of high-Cl coals, the corrosion rate increased consistently with increasing metal temperature, and the increases in the corrosion rate were quite significant. The corrosion rate was about 120 mpy at 1100°F; and about 250 mpy at 1200°F.

In general, the data showed no correlation between the rate of corrosion and the chlorine content in coal. The results showed a correlation between the rate of corrosion and the metal temperature used. Within the range of the metal temperatures used, a greater corrosion rate was observed at the higher metal temperature. In addition, the corrosion rates observed for the British coal appeared to be slightly greater than those of the two Illinois coals.

Summary and Conclusions

The results of pilot-scale combustion tests showed no correlation between the coal Cl content and rate of corrosion, but showed a correlation of the rate of corrosion with the metal temperature used. The corrosion rate was increased with an increase in the metal temperature during the combustion for all three coals. These data suggested that the different field history of the corrosivity caused by burning high-Cl Illinois coal and high-Cl British coal might have been the result of different superheater/reheater metal temperatures used in the US and UK utility boilers. These data could provide a basis for lifting the limit of burning high chlorine Illinois coals in the utility boilers.

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Table 1. Partial composition of 304SS superheater alloy in wt%

Element	C	Mn	P	S	Si	Ni	Cr
%	≤0.08	≤2.0	≤0.04	≤0.03	≤0.75	8-11	18-20

The balance of the alloy is Fe.

Table 2. Test matrix for pilot scale stoker boiler combustion

Test	Coal Sample	Metal temperature*
A	High-Cl IL coal	1100°F
B	High-Cl IL coal	1200°F
C	High-Cl British Coal	1100°F
D	High-Cl British Coal	1200°F
E	Low-Cl IL Coal	1100°F
F	Low-Cl IL Coal	1200°F

* Actually, the rate of corrossions were measured for four temperatures within a range from 1000 to 1200°F.

Table 3. Total chlorine, total sulfur, and ash content of the three coals.

wt % dry coal basis	High-Cl IL Coal	High-Cl British Coal	Low-Cl IL Coal
Total Chlorine	0.44	0.46	0.14
Total Sulfur	1.22	1.32	4.48
Ash	7.90	23.56	9.38

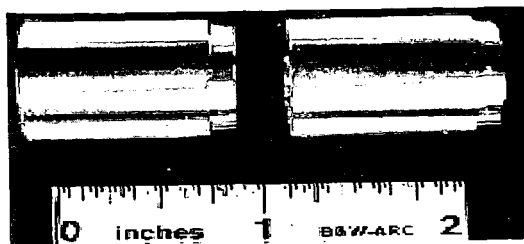


Figure 1: Arrangement of the chamfered tube segments on the corrosion probe

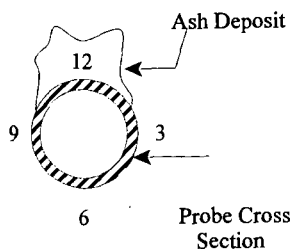


Figure 2. Illustration of the probe cross section, the leading edge (12:00 position), and the 30° to 90° area away from the leading edge for corrosion rate measurement

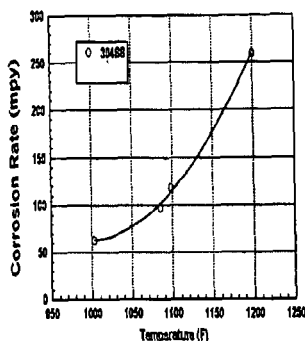


Figure 3. Corrosion rate (the greatest value) versus temperature at the positions between 30° and 90° for the test burning the high-Cl Illinois coal.

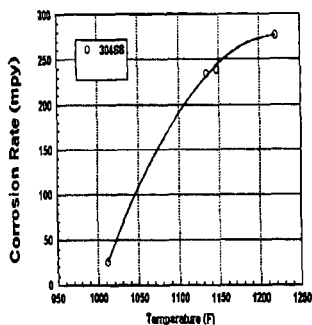


Figure 4. Corrosion rate (the greatest value) versus temperature at the positions between 30° and 90° for the test burning the high-Cl British coal.

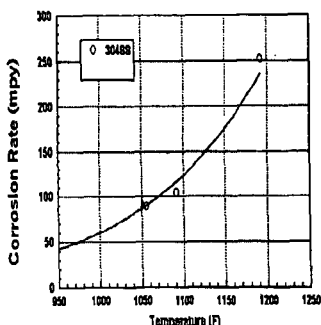


Figure 5. Corrosion rate (the greatest value) versus temperature at the positions between 30° and 90° for the test burning the low-Cl Illinois coal.